ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Organized by

T. Zachry

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 28 – April 1, 2004

INFLUENCE OF CALCITE SOLIDS AND DISSOLVED CALCIUM ON U(VI) SORPTION AND DESORPTION IN HANFORD SUBSURFACE SEDIMENTS

Wenming Dong[1], William P. Ball[1], Alan T. Stone[1],
Jing Bai[1], Chongxuan Liu[2] and Zheming Wang[2]
[1]Department of Geography and Environmental Engineering, Johns Hopkins University, 313 Ames Hall, 3400 North Charles Street, Baltimore, MD 21218
[2]Pacific Northwest National Laboratory, Environmental Dynamics and Simulations, Richland, WA 99352
wenming@jhu.edu; fax: 410-516-8996

INTRODUCTION

Uranium (VI) is a ubiquitous contaminant at Hanford and other DOE sites, resulting from its central role in the nuclear fuel cycle. In-ground migration of uranium (VI) at Hanford, WA, and other DOE sites is controlled by sorption and desorption processes with numerous different mineral solids possessing a range of material properties. Hanford vadose zone porewater and groundwater is generally in equilibrium with calcite that exists as a minor mineralogic component of all subsurface sediments. The purpose of this study is to experimentally investigate the influence of calcite and dissolved Ca on the sorption and desorption of U(VI) by means of batch systems using both Hanford sediment material and laboratory-grade calcite samples.

MATERIALS AND EXPERIMENTAL METHOD

The Hanford materials studied include a composite of clay/silt sediments (Hanford Silt Composite, HSC) and a composite of fine sands (Hanford Find Sand Composite, HFSC), both of which were prepared by PNNL colleagues from core samples. HSC was collected from the Plio-pleistocene layer between the Hanford and Ringold formations (42 - 44 m bgs (below ground surface)). The HFSC composite sample was obtained from the Hanford formation at depth from 19.1 to 29.3 m bgs.

Batch sorption studies were conducted with U(VI) concentrations ranging from $0.12 \times 10^{-6} - 12\times10^{-6}$ mol/L and pH ranging from 7.2 to 10 at 22.5 ^oC under a constant partial pressure of CO_2 ($P_{CO2} = 10^{-3.5}$ atm), and ionic strength (I = 0.05). The aqueous phase comprised calcite-saturated water with Na_2CO_3-$NaHCO_3$ or HNO_3 addition for pH control and $NaNO_3$ as support electrolyte. Studies were conducted with the original HSC and HFSC as well as with carefully split sub-fractions that included only the silt and clay size fractions, only the sand size fraction and carbonate free (acetic-acid-treated) material (Zachara *et al*., 2002) from the silt/clay fraction.

RESULTS AND DISCUSSION

The primary results indicate that a sorption "equilibrium" of U(VI) with the silt/clay fraction was established rapidly (within approximately 30 minutes) and that U(VI) distribution coefficients were independent of the solid/liquid ratio and independent of U(VI) concentration for concentrations above 10^{-6} mole/L. The sorption and desorption behavior of U(VI) on the original samples was quite similar to that on the silt/clay fraction and on pure calcite minerals, on a mass basis (See Table 1 and Figure 1). The carbonate-free silt/clay fraction was found to have a higher sorption affinity for U(VI) (See Figure 1), which suggests that calcite or other removed phases may cover or block access to higher affinity sorption sites for U(VI).

Table 1. Comparison of U(VI) sorption and desorption coefficients on different solid fractions of HSC and calcite with 3 days of sorption and desorption time at an initial U(VI) concentration of 1.2×10^{-6} mol/L under I= 0.05($NaNO_3$), pH=8.4±0.1, $P_{CO2}=10^{-3.5}$ atm and 22.5 ^oC.

Solid	Solution	Sorption K_d	Desorption K_d
Original HSC	Calcite saturated	17±1	22±1
Silt/Clay	Calcite saturated	18±1	23±1
Carbonate-free silt/clay	Calcite saturated	35±4	58±1
Carbonate-free silt/clay	$NaHCO_3$ solution	36±4	57±1
Sand	Calcite saturated	6±1	14.5±0.5
Calcite	Calcite saturated	18±2	22±1

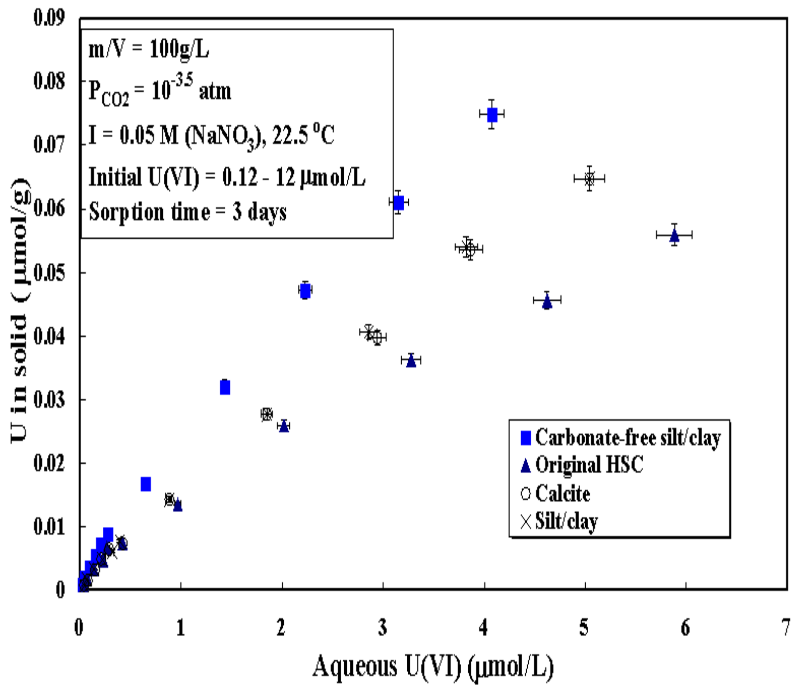

Figure 1. Sorption isotherms of U(VI) as a function of U(VI) concentration on different solid fractions of HSC and calcite at pH = 8.4 ± 0.1.

An especially interesting observation was that, for these calcite-saturated aqueous conditions, the sorption of U(VI) on silt/clay fraction of HSC exhibited a maximum sorption (See Figure 2) at pH = 8.4±0.1, with decreased sorption at both lower and higher pH ($P_{CO2} = 10^{-3.5}$ atm and I = 0.05) and with negligible sorption at pH < 7 or > 10 (solid:liquid ratio = 100 g/L). Results obtained in the range of pH 7.0 to 8.0 are in stark contrast with results from prior studies in calcite-free systems (Waite *et al*., 1994; Barnett *et al*., 2002), which found strong U(VI) sorption in this range. Independent calculations of aqueous U(VI) speciation (Grenther *et al*., 1992) under the given water conditions show that the aqueous complex of $Ca_2UO_2(CO_3)_3$ (Kalmykov and Choppin, 2000) should dominate at pH below 8.4 and that the aqueous complex of $UO_2(CO_3)_3^{4-}$ should dominate at pH above 8.4. The U(VI) speciation of the aqueous phase will be experimentally tested by applying laser-induced fluorescence spectroscopy at the temperature of liquid helium.

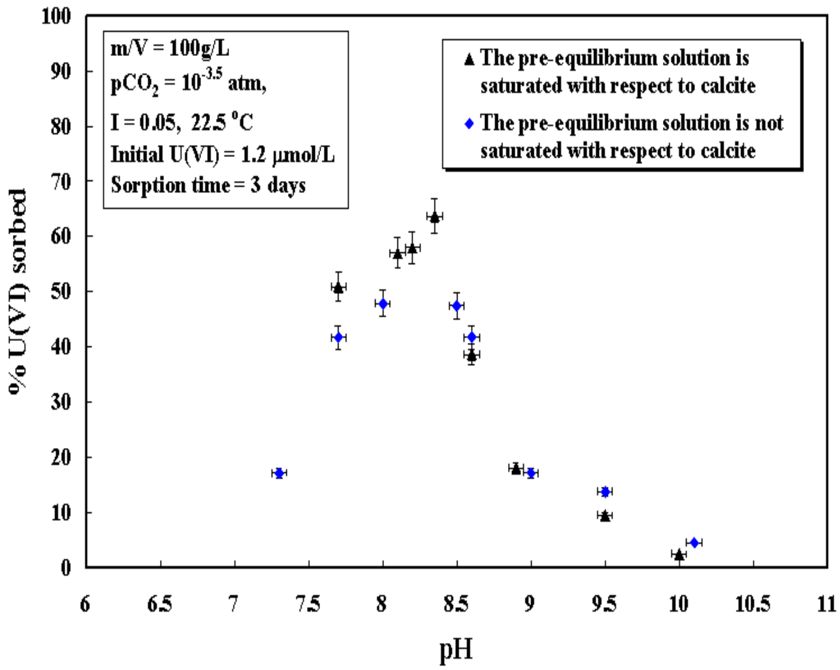

Figure 2. U(VI) sorption as a function of pH on silt/clay size fraction of HSC.

Given that the maximum sorption occurred at the approximate pH_{ZPC} for calcite (8.4) (Cappellen *et al*., 1993), one conceivable explanation for low-pH results is that carbonate coverings could be dominant sorbing phases at the U(VI) concentrations studied (>1 µM) and that the $Ca_2UO_2(CO_3)_3$ species does not strongly associate with positively charged surfaces. In any case, the results clearly show that U(VI) sorption in calcite-saturated systems is lower at pH 8.0 than what has previously been observed in previous studies with calcite-free systems. Overall, the results clearly show that U(VI) transport under calcite-saturated systems will be a strong function of pH, with sorption at pH<8.4 being far less extensive than would be predicted if calcium were not considered.

ACKNOWLEDGEMENTS
This research was supported by the Environmental Management Science Program of the office of Science, U.S. Department of Energy under contract DE-FG07-02ER63498. The authors also wish to thank Steven C. Smith at Pacific Northwest National Laboratory (PNNL) for providing the Hanford subsurface sediments. The research was also supported by Environmental Molecular Science Laboratory (EMSL) at PNNL.

REFERENCES
1. Zachara, J.M., Smith, S.C., Liu, C., McKinley, J.P., Serne, R.J. and Gassman, P.L., (2002) *Geochim. Cosmochim. Acta* **66**, 193-211.
2. Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A. and Xu, N., (1994) *Geochim. Cosmochim. Acta* **58**, 5465-5478.

3. Barnett, M.O., Jardine, P.M. and Brooks, S.C., (2002) *Environ. Sci. Technol*. **36**, 937-942.
4. Grenther, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., and Wanner, H., (1992) Chemical Thermodynamics. Vol. 1 *Chemical Thermodynamics of Uranium*. OECD-NEA, Elservier.
5. Kalmykov, S.V. and Choppin, G.R., (2000) *Radiochim Acta* **88**, 603-606.
6. Cappellen, P.V., Charlet L., Stumn, W. and Wersin, P., (1993) *Geochim. Cosmochim. Acta* **57**, 3505-3518.